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Crystallization and structure of a MgO-Al_2O_3-SiO_2-TiO_2 glass-ceramic

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The structure and changes occurring during the volume crystallization of a MgO-Al_2O_3-SiO_2-TiO_2 glass induced by heat-treatment at temperatures in the range 740 to 1300°C were investigated by means of DTA, scanning electron microscopy, X-ray diffraction, electron microprobe analysis, density and other measurements. Crystallization proceeds by liquid phase separation and coalescence of small particles forming larger microcrystalline regions dispersed in the glassy phase, these regions fill the bulk of the glass during the heat-treatment. Such a mechanism of crystallization leads to the formation of a fine-grained homogeneous structure whose chemical composition is identical to that of the glassy matrix (as is shown by the electron microprobe). The scanning electron microscope revealed two crystalline phases in the initial stage (850 to 890°C) of crystallization while X-ray diffraction identified only a μ-cordierite type structure, which at temperatures above 1100°C is transformed into the α-form. The X-ray diffraction patterns showed further that a cordierite $2MgO.2Al_2O_3.nSiO_2$ solid solution may be formed dependent on the heat-treatment temperature. Stereoscan micrographs of various stages of crystallization show the development of the glass-ceramic. In addition, the influence of the technique employed to prepare the electron microscope specimens, on their surface topography is also shown.

1. Introduction

The controlled nucleation and crystallization of glass leading to its conversion into microcrystalline glass-ceramic has received considerable attention in recent years. This is so because the microcrystalline materials produced during heat-treatment of special glasses exhibit many remarkable physical and mechanical properties and have varying practical applications. Moreover, the investigations of the initial stages of nucleation and crystallization are also of wide theoretical importance because they help in understanding the mechanisms of phase transformations not only in ceramic systems.

An understanding of the dynamic process taking place during the high-temperature solid state conversion of a vitreous to a crystalline material requires the use of a variety of techniques including DTA, scanning electron microscopy, X-ray diffraction, electron microprobe analysis and others. In this paper, the process of crystallization of a MgO-Al_2O_3-SiO_2 glass containing TiO_2 as a nucleating catalyst has been investigated by such methods. The presence of TiO_2 causes glass-in-glass separation and furthermore leads to crystallization of cordierite.

The nomenclature describing the structural changes of cordierite is the same as the one used by Karkhanavala and Hummel [1].

2. Mechanism of catalysis

It is known that catalysed crystallization of glass comprises two distinct stages proceeding during the heat-treatment of glass, i.e. formation of nuclei and subsequent crystallization on preformed sites. According to Kingery [2] and Stookey [3] one of the possibilities for promoting nucleation is the precipitation during cooling of the catalyst dissolved in the glass thus giving rise to nuclei for crystallization of other phases. An example of such a process is the precipitation of metal particles in photo-sensitive glasses. Another possibility of promoting crystallization is metastable immiscibility occurring in originally homogeneous glass, with which we are concerned here. The immiscibility may occur during cooling of the melt, or during reheating of the quenched glass. Depending on glass composition and tem-

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perature conditions, the phase separation may be induced either by spinodal decomposition (continuous process), or by nucleation and growth (discontinuous process) [4]. The separated phase usually appears in the form of dispersed droplets (emulsion) in the glassy matrix. The arrangement of atoms in one of those phases may be more ordered than in the initial glass. This metastable phase will then crystallize during reheating of the glass. The crystalline particles with colloidal dimensions formed in the metastable phase, heterogeneously nucleate crystallization of further phases. An example of the above stated mechanism of crystallization is given in the work of Doherty *et al* [5] on Li_2O-Al_2O_3-SiO_2-TiO_2 glasses. In this work the following sequence was observed: the separation of two glassy phases; the formation of crystalline nuclei of $Al_2Ti_2O_7$ some 50 Å in size, presumably in one of the glass phases; and afterwards crystallization of β-eucriptite.

One of the common catalysts used in the manufacture of glass-ceramics is titanium dioxide. The crystallization process induced by titania has not been entirely explained yet. Originally it was thought that small crystallites of TiO_2 precipitate during heat-treatment and form heterogeneous crystallization sites [6]. However, such an explanation is not always satisfactory: it has been demonstrated by X-ray diffraction that in many glasses containing TiO_2 phases other than rutile or titanate crystallize first and indeed the presence of rutile and titanate is only detected towards the end of the crystallization [7,8]. On the other hand, when TiO_2 was missing, the glasses obtained either did not crystallize or at most underwent only surface devitrification [8-10]. The failure to observe titania as the first crystalline phase has led workers to suggest another mechanism of nucleation.

Hinz and Kunth [11] for example suggested that TiO_2 produces glass-in-glass immiscibility, and that one of the phases then crystallizes during the heat-treatment. Phase separation in the glass containing TiO_2 was also observed by Ohlberg *et al* [8], Kondratiew [12] and Hillig [13]. It has been established that the separation of two phases appears during the precrystalline period of the MgO-Al_2O_3-SiO_2-TiO_2 glass, one of which is probably enriched in TiO_2. The tendency of titanium dioxide to cause phase separation may be explained by considering the structural role of titanium ion. The Ti^{+4} ion, due to its ion radius size being 0.68 Å assumes an intermediate role between glass formers and modifiers in the structure of glass [14]. Therefore, at least a part of the Ti^{+4} ion should appear with co-ordination number 6. However, if it is to take part in the formation of glassy network, it should possess a co-ordination number not higher than 4. Weyl [15] supposes that the Ti^{+4} ion may change its co-ordination number from 4 to 6 on cooling from high temperatures. Thus in some cases, the TiO_2 may be displaced from the silicon-oxygen network and appear as a separated phase, possibly combined with another oxide. The co-ordination number, however, depends not only on temperature but also on the composition of a system, and may have the value 4 or 6, or the two co-ordination numbers may exist simultaneously.

TABLE I Weight and mol % of glass constituents

	Wt %	Mol %
SiO_2	64.8	65.6
Al_2O_3	18.5	11.0
MgO	9.3	14.0
TiO_2	7.4	9.4
Fe_2O_3*	0.2	—

*By analysis

3. Experimental procedures

3.1. Preparation and heat-treatment of the glass

The investigated glass was derived from the MgO-Al_2O_3-SiO_2-TiO_2 system and has the composition stated in Table I. The batch was prepared from pure (reagent grade) raw materials such as: quartz, Al_2O_3, $MgCO_3$, TiO_2. The thoroughly mixed and precalcined raw materials were melted in Pt-Au crucibles in an electric furnace at 1500°C for 7 h, and then cooled to room temperature within a few minutes.

To cause crystallization, the glass was then heat-treated for 1 h at various constant temperatures between 740 and 1300° C, and quenched. More details about each heat-treated specimen and the analysis carried out on them are given in Table II.

3.2. General description of methods

Differential thermal analysis was used in order to follow the changes occurring during heat-treatment of the glass and thus to determine the

TABLE II Analysis performed and changes detected in the glass after each heat-treatment cycle

No.	Temperature of heat-treatment (°C)	Analysis performed	Remarks
1	Original, not heated glass	DTA	Yellowish colour
2	740	—	Blue-violet colour
3	760	—	Blue-violet colour
4	800	Xrd, sem.	Opalescence
5	850	Xrd, sem, emX	μ-cordierite
6	875	Xrd, sem, emX	μ-cordierite
7	890	Xrd, sem, —	μ-cordierite
8	930	Xrd, sem, —	μ-cordierite
9	1000	Xrd, sem, —	$\mu + \alpha$ cordierite
10	1100	Xrd, ——	$\mu + \alpha$ cordierite
11	1200	Xrd, ——	$\alpha + \mu$ cordierite
12	1300	———	Partially melted

Description:
DTA, differerential thermal analysis
Xrd, X-ray diffraction
sem, scanning electron microscopy
emX, electron microprobe X-ray analysis

temperatures of nucleation, crystallization and melting of the glass ceramic. The analysis was made in the range 20 to 1050°C using powdered sample together with powdered alumina as an inert reference material. The rate of heating was 10 deg per min.

The phases which crystallized during heat-treatment of the glass were identified by means of X-ray diffraction analysis. This was accomplished by quenching the samples from selected temperatures up to the maximum. They were then crushed into fine powder and examined with a diffractometer* using Cu$K\alpha$ radiation with a Ni filter.

The structures of the crystallized glass-ceramics were observed by means of a scanning electron microscope† permitting direct observations of surface topography. The samples were prepared by diamond polishing or by fracturing, and some of them were etched in 1% hydrofluoric acid. Next they were covered by evaporation of a thin layer of Cu to avoid charging by the electron beam. All observations have been performed with an accelerating voltage of 20 kV, and with an angle of tilt of about 45° between the specimen and the electron seam. More details about the preparation technique and description of the microscope are given in a previous publication [16].

In order to determine the concentration and distribution of elements in the glassy matrix as well as in the separated phase, and at the same time to establish the influence of TiO_2 on phase separation, an electron microprobe X-ray analyser** was used. The specimens were prepared as for scanning electron microscope observations.

Thermal expansion measurements were carried out in a differential dilatometer with a heating rate of 10 deg per min. Finally the densities and softening temperatures of the glass-ceramics were determined, and some infrared absorption measurements were carried out.

3.3. Results

3.3.1. Physical properties of glass-ceramic

The original cast glass is transparent with a slight golden colour which probably originates from TiO_2 and small amounts of Fe_2O_3 present as impurities. The appearance of the material gradually changes with heat-treatment. Annealing within the temperature range 740 to 800°C develops an intense blue-violet colour, and raising the temperature to 850 to 900°C brings about the appearance of opalescence and slight turbidity. Both the change of colour and increasing turbidity are light scattering effects and give evidence of changes occurring in the glass. The increased absorption in the blue and violet part of the spectrum suggests partial reduction of Ti^{+4} to the Ti^{+3} state [17,23] which results in rearrangement of glass structural units and leads to phase separation. In this separated form one of the phases has a different composition than the other. Further increase of the temperature to 1100°C produces a non-transparent, microcrystalline material of a grey colour.

The softening of the crystalline glass-ceramic occurs at about 1270°C as determined by a microscope with a heating stage. The softening point of the original glass could not, however, be established because of rapid crystallization

*Made by Philips.
†"Stereoscan", Cambridge.
**Applied Research Laboratories Inc.

preventing the deformation of the specimen.

The average thermal expansion coefficient over the temperature range 20 to 600°C of a specimen crystallized at 930°C – i.e. consisting of μ-cordierite – is $28.7 \times 10^{-7}/°C$.

The densities of specimens heat-treated at various temperatures, are as follows: original glass, 2.469; 760°C, 2.488; 800°C, 2.487; 930°C, 2.586; 1200°C, 2.495 g/cm^3. The tendency of the density to increase and then decrease during the crystallization process has been observed in glass-ceramics of similar chemical composition but markedly different phase composition by Ziemba [18] and Kumar [19].

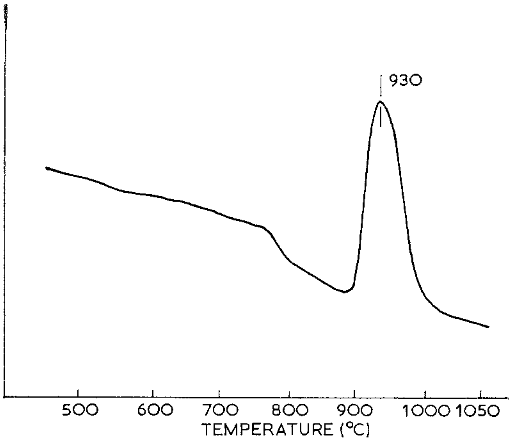


Figure 1 Differential thermal analysis of the glass during crystallization.

3.3.2. *Differential thermal analysis*

A DTA record for the glass during heating from 300 to 1050°C is given in Fig. 1. A shallow endothermic dip is observed over the temperature range 800 to 900°C and this is associated with annealing and nucleation of the uncrystallized glass. The marked exothermic peak beginning at 910°C and reaching a maximum at 930°C is attributed to crystallization of μ-cordierite, which was confirmed by X-ray diffraction (Fig. 8). Above 1100°C (above the maximum working temperature of the apparatus) another maximum would be expected to occur due to the polymorphic transformation of μ-cordierite to the α-form, and an endothermic effect at 1270°C should be observed due to melting of the glass-ceramic.

3.3.3. *Scanning electron microscopy*

Figs. 2 to 7, which show scanning electron micrographs of glass specimens heat-treated at temperatures from 800 to 1000°C, illustrate the gradual change in structure from separation to crystallization.

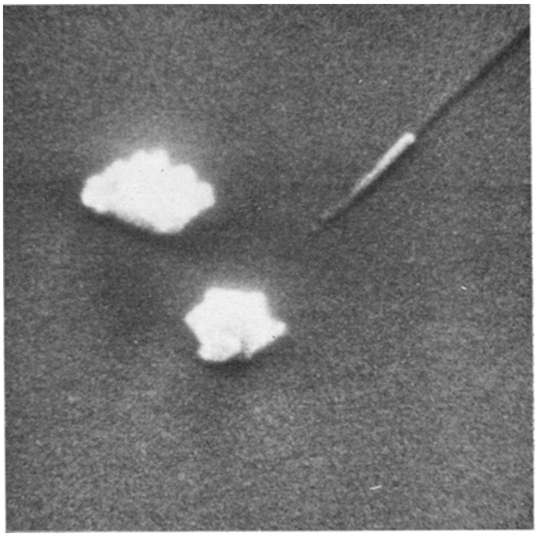


Figure 2 Unetched fractured surface of glass annealed at 800°C. Slight granular differences seen on the surface indicate the initiation of the droplet separation process in glass. The white grains are broken pieces of glass. Stereoscan micrograph, magnification × 23000.

Fig. 2 shows fractured surface topography of the glass heat-treated at 800°C. The white chips seen on the surface are broken pieces of glass. No two-phase structure is observed at this stage of heat-treatment by this technique, although a slight granularity of the glass surface may be detected. Previous experience shows that coarser granulation on the fractured surface indicates inhomogeneities in the structure of the glass and may be attributed to the onset of the droplet separation process [20]. X-ray diffraction did not provide evidence for the presence of any crystalline phase.

From the next figure it is apparent that raising the temperature to 850°C causes distinct phase separation and, as shown by X-ray diffraction, the onset of crystallization. Fig. 3a shows an unetched fractured surface of the modified glass and Fig. 3b shows a surface of the same glass polished and etched with 1% HF acid. The two phase structures can be clearly seen on both micrographs. The semi-spherical elevations and depressions, 5 to 10 μm in diameter, with tails emanating from each droplet, observed in Fig. 3a, are the dispersed phase. This tail-

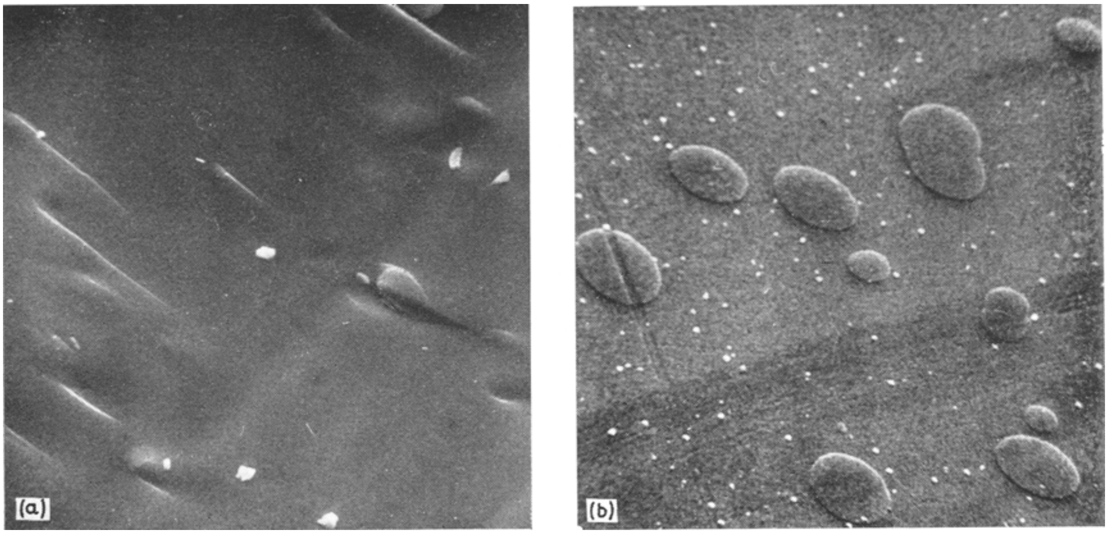


Figure 3 The glass-ceramic after heat-treatment at 850° C, showing droplet-shaped separation areas; (*a*) unetched fractured specimen, × 1020, (*b*) polished and etched specimen, × 1300.

like structure was caused during fracturing by propagation of the crack front in the interface between the separated phase and the matrix, and indicates the movement of the fracture front which was diagonally from left to right [21].

By applying the technique of polishing and etching the samples, the round shape of the droplets and their distribution in the matrix can be seen as shown in Fig. 3b. The less acid-resistant glassy matrix has been partially removed by etching, thus giving the relief on the surface.

In view of the simultaneous development of X-ray diffraction patterns (Fig. 8) it is likely that the large round droplets are crystals or crystalline aggregates. In addition, from the optical microscope observations it is apparent that the round droplets are anistropic and show spheroidal extinction of light, while the surrounding matrix is isotropic.

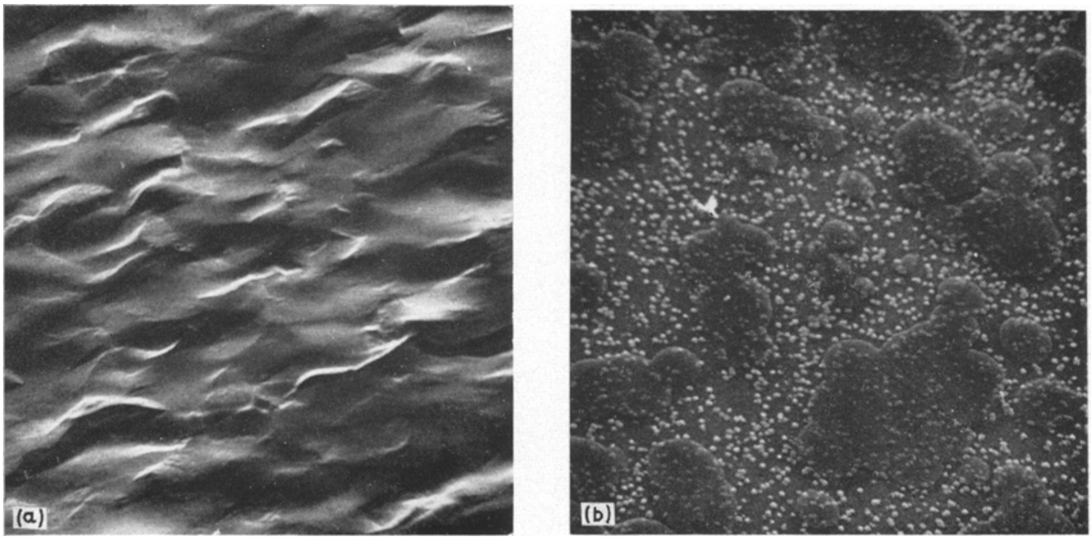
The advanced state of separation and crystallization due to heat-treatment at 875° C is shown in Fig. 4. The surface topography of this fractured specimen shows more diversity than that of specimens heated at lower temperatures (shown on preceding figures), indicating that the fracture has propagated through an increased number of interfaces.

On the polished and etched specimen (Fig. 4b), round areas extending to several microns, partially impinging on one another can be seen. Evidently, the crystallization proceeds beyond the phase boundary. The areas concerned are probably crystal aggregates of μ-cordierite. It is of interest to note that structures of both phases shown in high magnification (Fig. 4c), i.e. the separated, microcrystalline droplets, as well as the glassy matrix, are similar to each other and consist of small (0.05 to 0.1 μm) microheterogeneities. Moreover, the morphology of the dispersed phase seems to be slightly more compact than the morphology of the matrix.

It should be borne in mind, however, that in spite of direct observations of specimens in the scanning electron microscope, the submicrostructure just described was revealed indirectly by chemical etching, which may have had an influence on the results. In this specimen a further phase appears in the form of small, light inclusions with dimensions less than 1 μm, which at high magnification are seen to have a star-like shape. Nevertheless, the only crystalline phase detected by X-ray diffraction was μ-cordierite.

Fig. 5 demonstrates a further microstructural change by heat-treatment at 890° C. The ceramic process is brought to an end by conglomeration of adjacent crystalline areas.

Small crystals of μ-cordierite formed in the



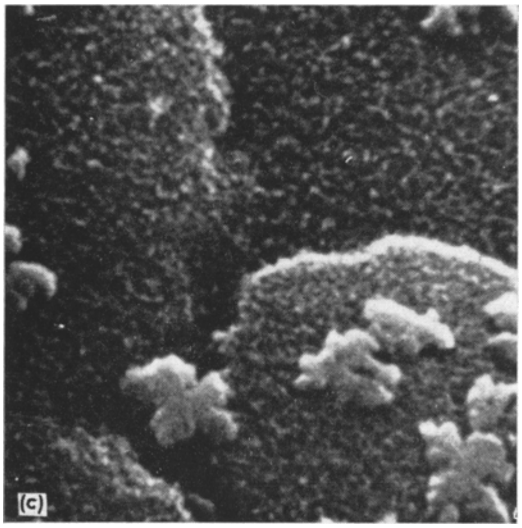


Figure 4 Advanced state of separation and crystallization due to heat-treatment of the glass-ceramic at 875° C. The separated areas are microcrystalline aggregates of μ-cordierite; (a) etched fractured surface, × 1100, (b) polished and etched surface, × 1200, (c) magnified fragment of picture 4b, × 24000.

sample heat-treated at 930° C are shown in high magnification in Fig. 6 (polished, etched specimen).

Finally, Fig. 7 shows an unetched, fractured surface of the glass-ceramic crystallized at 1000° C. The smooth glassy areas may be differentiated from those which are microcrystalline.

3.3.4. X-ray diffraction

The results of the X-ray diffraction analysis are presented in Fig. 8. Heating of the glass at 800° C did not cause crystallization detectable by X-ray examination. The diffractogram A obtained shows no diffraction patterns and is typical of an amorphous material.

The first crystalline traces, identified as μ-cordierite, appeared after heat-treatment at 850°C, as is shown by the weak maxima on diffractogram B.

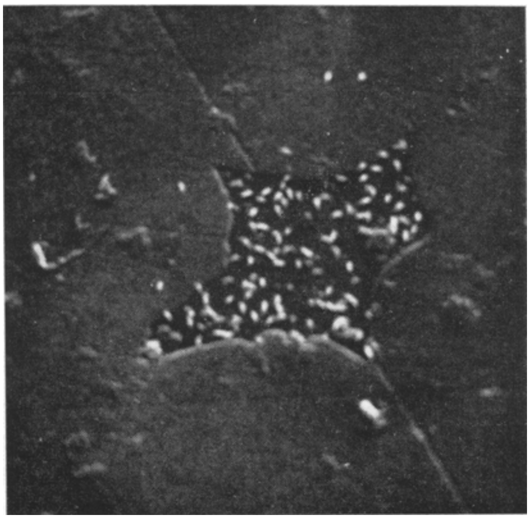


Figure 5 Agglomeration of microcrystalline aggregates due to heat-treatment at 890° C. Polished, etched specimen × 3000.

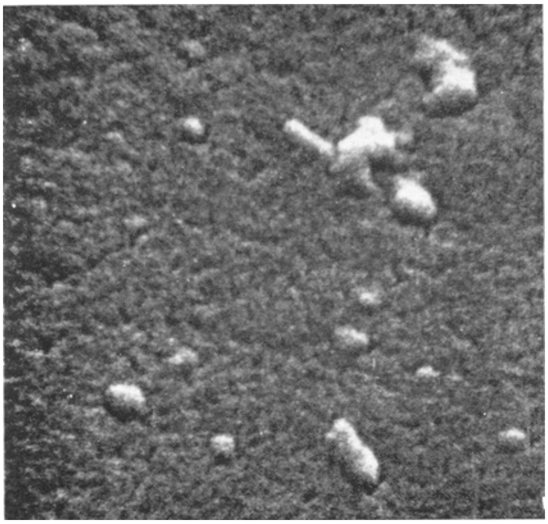


Figure 6 Small, randomly orientated crystals of μ-cordierite present in glass-ceramic heat-treated at 930° C. Polished, etched sample, × 24000.

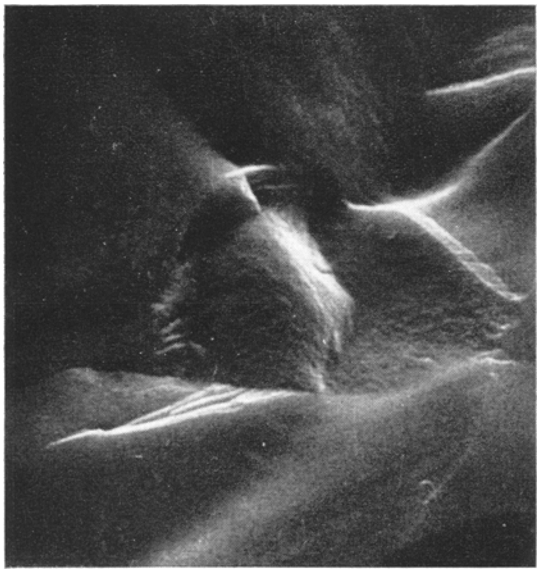


Figure 7 Unetched fractured surface of glass-ceramic heat-treated at 1000° C. The glassy areas (smooth) may be differentiated from those which were crystalline (coarse) at fracture, × 2800.

Heating at 890 and 930° C, the latter being the temperature corresponding to an exothermic effect detected by the DTA analysis, resulted in increased crystallization which is shown by larger maxima and a decrease of the background intensity in the diffractograms C and

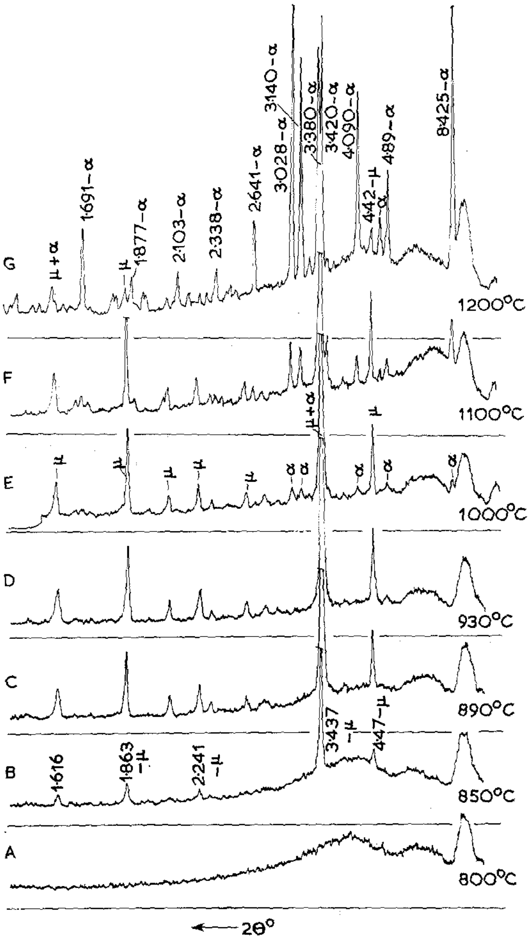


Figure 8 X-ray diffraction patterns of the glass heat-treated at various temperatures.

D, respectively. The only crystalline phase appearing was μ-cordierite, the amount of which was at least 50%.

At about 1000° C, μ-cordierite begins to transform to the high temperature α-form and several new maxima of low intensity corresponding to α-cordierite appear. During heat-treatment at 1100° C further transformation of μ-cordierite proceeds with the appearance of stronger peaks of α-cordierite, although the main maxima still originate from the μ form (diffractogram F).

Finally, the glass-ceramic heat-treated at 1200° C consists of two crystalline phases, i.e. μ- and α-cordierite, with α-cordierite as the dominant phase (diffractogram G).

At the same time, the X-ray diffractometer traces of these materials showed slight shifts of the entire diffraction pattern toward higher

Bragg angles with increasing temperature of heat-treatment, as is shown in Fig. 9. Such changes in the positions of the diffraction peaks indicate changes in the structure of μ-cordierite, and, in particular, since the composition of the glass is silica-rich, they may suggest the formation of a solid solution of cordierite with silica.

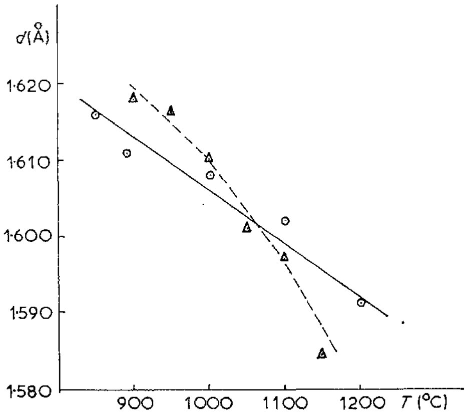


Figure 9 Diagram showing the change of lattice spacings of crystallizing μ-cordierite with heat-treatment. Cu$K\alpha$ radiation. The dotted line was obtained with a high temperature X-ray camera.

3.3.5. Electron microprobe analysis

It has been established that the catalysed crystallization of glass is the basic process in the production of glass-ceramic. It was therefore of interest to investigate the process of nucleation and the initiation of crystallization in greater detail. It is evident from previous work and from the results of this investigation that the nucleation and crystallization of MgO-Al_2O_3-SiO_2 glasses in the presence of TiO_2 as a catalyst, proceeds by phase separation. Since the areas of the phase separation in the specimens were several microns in diameter, the use of the electron microprobe (permitting analysis of a volume of 1 μm^3) to determine differences in concentrations of Si, Mg, Al, Ti and O seemed to be promising.

The specimens used had been heat-treated in the annealing temperature range, i.e. 850 and 875°C, and showed phase separation. They were prepared for microanalysis in a similar way as for the scanning electron microscope observations, i.e. by polishing with subsequent etching or by fracturing, and finally coated with Cu. The analyses were carried out by observing the display of $K\alpha$ signals on an oscilloscope screen, or by point-to-point integration, using the step scanning stage drive with automatic counting of pulses over a fixed period of time.

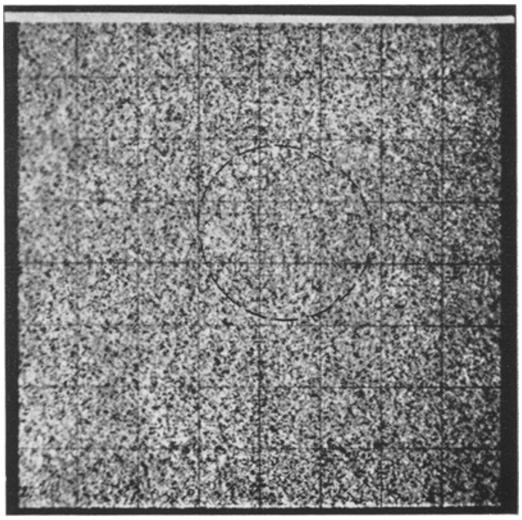


Figure 10 Uniform distribution of Ti$K\alpha$ radiation in the glass heat-treated at 850°C, exhibiting phase separation. The dotted line shows the phase boundary as on the back-scattered electron picture.

However, no differences could be detected between concentrations of elements in the matrix and in the separated areas in any specimens, as shown for example in Fig. 10, which is an oscillogram for Ti$K\alpha$ radiation. The dotted line shows the boundary of the separated phase. The absence of concentration differences between the bulk glass and the separated phase, indicated by the microprobe, is surprising since X-ray diffraction analysis of the same samples showed the presence of μ-cordierite, the composition of which differs considerably from the constitution of the initial glass.

From the scanning electron microscope observations, it seems possible that the round droplets are aggregates of microcrystalline μ-cordierite. These aggregates are composed of small crystals (of the order 500 to 1000 Å) surrounded by a glassy phase, and they form larger areas in the glass matrix, seen on electron micrographs as regions with positive relief. The electron microprobe results may thus perhaps be explained as follows.

Owing to the very small crystal dimensions in the separated aggregates it is possible that the microprobe, with a beam diameter of approximately 1 μm, is unable to detect differences in the X-ray intensities from the crystallites and the surrounding glass. It therefore yields only the average concentrations of the elements, which in the sectors of 1 μm in the separated areas are similar or equal to those in the surrounding glass matrix.

4. Discussion of results

The first changes associated with nucleation of the MgO-Al_2O_3-SiO_2-TiO_2 glass proceed during heat-treatment at temperatures between 740 and 800°C. At the beginning they could be observed only by means of the change in colour and the increase of the density from 2.469 g/cm^3 for the initial glass to 2.487 g/cm^3 for the glass annealed at 800°C. The change in colour is caused by partial reduction of Ti^{+4} to Ti^{+3} which results in microseparation of phases and the gradual appearance of opalescence. One of the phases is probably enriched in titanium dioxide. The increase of the density, on the other hand, gives evidence for the aggregation of atoms and gradual arrangement of the glass structure. At this stage of heat-treatment no crystalline phase was detected by X-ray diffraction.

The onset of phase separation observed in glass heat-treated at 800°C is associated with the formation of small heterogeneities, less than 500 Å, formed due to internal nucleation. These microheterogeneities might have some periodic order, pseudocrystalline form and chemical composition approaching that of μ-cordierite which crystallizes at higher temperatures. The heterogeneities undergo coalescence and better structural arrangement during heat-treatment and transform into a crystalline form, forming crystal aggregates.

The formation of the aggregates is observed by SEM and X-ray diffraction in the glass heat-treated at 850°C as a distinct phase separation, with simultaneous appearance of a small amount of the crystalline phase μ-cordierite. The separated phase appears in the form of dispersed spherical areas surrounded by the bulk glass. This phase is almost completely crystalline and contains grains of μ-cordierite 500 to 2000Å in size, which are enclosed by the residual glass thus forming spherical agglomerations in the bulk glass, several microns in size. The dimensions of the crystals in the aggregates are similar to those of the previous heterogeneities. At the beginning, the coalescence and crystallization proceeds at the point of contact of several adjacent pseudocrystalline particles and then at the interfaces between the aggregates thus formed and the glassy matrix. This leads to a rapid differentiation in size of the individual aggregates.

The above-stated mechanism of crystallization is supported by the similarity of the structures of the two separated phases as observed in the scanning electron microscope. This is shown by the presence of similar heterogeneities appearing both in the crystalline phase and in the surrounding glass. The fine-structure so-formed explains, at the same time, a uniform concentration of elements in the μm sectors in the glassy as well as in the crystalline phase, as was shown by the electron microprobe.

The proposed homogeneously nucleated nature of glass also seems to be supported by infra-red absorption spectroscopy. The infra-red spectra (not shown here) of the original glass, the glass heat-treated at nucleation temperature range, and the glass-ceramics containing μ- and α-cordierite are all very similar, showing comparable absorption bands. This indicates the existence of Si—O bonds of a similar condensation ratio in the original amorphous glass and in the crystallized specimen, and, in particular, indicates the presence of microstructural elements related to $AlSi_5O_{18}$ rings of crystalline synthetic cordierite.

During heat-treatment at 875°C, the glass-crystal transformation proceeds, followed by an increase in the size of the aggregates and their mutual conglomeration. The growth of the aggregates proceeds by interaction with pseudocrystalline microheterogeneities located in the vicinity of their boundaries, rather than by increase of individual crystal dimensions.

Apart from the μ-cordierite-like phase present in the glass ceramic heat-treated at the temperatures 850 to 890°C, another phase appears in the form of small, uniformly dispersed star-like inclusions. An approximate comparison of the μ-cordierite diffraction pattern intensities with the amount of that phase observed in the microscope do not show a quantitative agreement. This phase probably disappears at higher temperatures.

Further increase of the heat-treatment temperature (890°C) causes an increase in the amount of the crystalline phase. The crystallization proceeds and the dimensions of the separated areas increase so that they almost completely fill the bulk glass. The main crystalline phase is the μ-cordierite formed at about 910°C, as determined by the DTA. That the first crystalline traces are formed already at 850°C, i.e. before the crystallization process becomes exothermic, is due to the fact that there is no distinct difference between the process occurring in the precrystalline period in glass and the first stage of crystallization, the whole process being continuous [22].

During heat-treatment at temperatures above 930°C, crystallization of μ-cordierite is completed, and, at temperatures above 1100°C, polymorphic transformation of μ-cordierite into the α form occurs. This is associated with a decrease in the density from 2.586 to 2.495 g/cm^3, due to a small increase in volume during the $\mu \rightarrow \alpha$ transformation.

From the scanning electron microscope and the optical microscope observations, it may be concluded that the glass-ceramic heat-treated at temperatures above 1000°C is highly crystallized and contains 80 to 90 vol % of crystalline phase, the rest being glass. This disagrees, however, with the chemical composition of the material which contains 18.5 wt % Al_2O_3. On the assumption that alumina is the constituent limiting the formation of cordierite $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$, the amount of cordierite formed cannot exceed 53.2 wt %. It seems likely that the discrepancy could be explained by the formation of a solid solution of cordierite with silica. The X-ray diffraction analysis shows a shift in the μ-cordierite patterns towards lower d-values for the specimens heat-treated at higher temperatures. This indicates changes occurring in the μ-cordierite structure, and, in particular, the possibility of substitution of the Si ions (of smaller radius) into sites in the lattice occupied by Al, thus diminishing the unit cell dimensions. The crystalline phase formed at elevated temperatures may be a silica-rich member of the solid solution series rather than pure cordierite of mole ratio 2:2:5.

To confirm this, a series of solid solutions of composition $2MgO \cdot 2Al_2O_3 \cdot nSiO_2$, where n was varied from 5 to 7, was prepared by glass devitrification. The glass devitrification technique was similar to that described previously [1] and involved double melting of batch compositions at 1570°C and then crystallization of the powdered glass (less than 75 μm (200 mesh)) by heat-treatment at 870°C for two weeks. X-ray diffractometer traces of these μ-cordierite-like materials showed a shift in the diffraction pattern towards lower d-values with increasing silica content, thus providing proof of the formation of solid solutions in specimens heat-treated at higher temperatures. A detailed investigation of the changes in the cordierite structure due to constitution as well as to thermal expansion is not, however, relevant to this study and will be undertaken at a later date.

Apart from the formation of the solid solution, there is also a possibility that the glassy phase may be occluded into the dendritic structure of the crystals, which would also contribute to an apparent decrease in the quantity of glass and to an increase in the apparent crystallinity.

Finally, the glass-ceramic heat-treated at 1200°C contains small crystals of both forms of cordierite, i.e. μ and α (or its solid solution), with the α-form as the dominating phase. At the same time, the X-ray diffraction analysis shows minute unidentified peaks.

At temperatures higher than 1200°C the samples soften and deform due to melting of the glass-ceramic.

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